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(12) **EUROPEAN PATENT APPLICATION**

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(54) A method of processing a nickel/titanium-based shape memory alloy and article produced therefrom.

(57) There is disclosed a method of processing a nickel/ titanium-based shape memory alloy. The method comprises overdeforming the alloy so as to cause at least some amount of nonrecoverable strain, temporarily expanding the transformation hysteresis by raising the austenite transformation temperature, removing the applied stress and then storing the alloy at a temperature less than the new austenite transition temperature. There is also disclosed a method of preassembling a composite coupling which includes the steps of overdeforming a driver member, removing the stress, engaging the driver member and an insert and them warming the driver and insert to a temperature less than A_s'. Finally, there are disclosed couplings produced by these methods.

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DESCRIPTION

5   A METHOD OF PROCESSING A NICKEL/TITANIUM-BASED SHAPE
MEMORY ALLOY AND ARTICLE PRODUCED THEREFROM

This invention relates to the field of processes
10   suitable for producing a nickel/titanium-based shape
memory alloy and a shape memory alloy article. This
invention further relates to the field of methods and
processes suitable for producing a
nickel/titanium-based shape memory alloy composite
15   coupling.

Materials, both organic and metallic, capable of
possessing shape memory are well known. An article
made of such materials can be deformed from an
20   original, heat-stable configuration to a second,
heat-unstable configuration. The article is said to
have shape memory for the reason that, upon the
application of the heat alone, it can be caused to
revert or attempt to revert from its heat-unstable
25   configuration to its original heat-stable
configuration, i.e., it "remembers" its original shape.

Among metallic alloys the ability to possess shape
memory is a result of the fact that the alloy undergoes
30   a reversible transformation from an austenitic state to
a martensitic state with a change of temperature.
Also, the alloy is considerably stronger in its

austenitic state than in its martensitic state. This
transformation is sometimes referred to as a
thermoelastic martensitic transformation. An article
made from such an alloy, for example, a hollow sleeve,
is easily deformed from its original configuration to a
new configuration when cooled below the temperature at
which the alloy is transformed from the austenitic
state to the martensitic state. The temperature at
which this transformation begins is usually referred to
as M_s and the temperature at which it finishes M_f.
When an article thus deformed is warmed to the
temperature at which the alloy starts to revert back to
austenite, referred to as A_s (A_f being the temperature
at which the reversion is complete), the deformed
object will begin to return to its original
configuration.

Commercially viable alloys of nickel and titanium
have been demonstrated to have shape-memory properties
which render them highly useful in a variety of
applications.

Shape-memory alloys have found use in recent years
in, for example, pipe couplings (such as are described
in U.S.P. 4,035,007 and 4,198,081 to Harrison and
Jervis), electrical connectors (such as are described
in U.S.P. 3,740,839 to Otte and Fischer), switches
(such as are described in U.S.P. 4,205,293 to Melton
and Mercier), etc., the disclosures of which are
incorporated herein by reference.

It is, of course, advantageous to have the alloy
austenitic at the service temperature which is often

but not necessarily near room temperature, since the austenite phase is stronger than the martensite phase. In fact, it would be desirable to have the alloy remain austenitic over a wide range of service temperatures,

5   for example from substantially below room temperature to substantially above room temperature, so that the alloy has practical utility.

As an illustration, Military Specification

10   MIL-F-85421 requires a product that is functional to about -55°C. If the product comprises a shape memory alloy, then for convenience in shipping the product in the heat-unstable configuration, the product should not recover prior to about 50°C. It is a matter of

15   commercial reality, within and without the military, that the product satisfy these requirements.

It is also desirable that the alloy be martensitic in the vicinity of room temperature so that the article

20   can be fabricated, stored, and shipped at or near room temperature. The reason for this is that in the case of an article made from the alloy, a coupling, for example, the article would not recover prematurely.

25   Conceptually, one way to achieve these desirable results, to wit, an alloy that is martensitic near room temperature and which is also austenitic over a large range of temperatures including room temperature, is to have an alloy which exhibits a sufficiently wide

30   tranformation hysteresis, say, greater than about 125°C. If the hysteresis were sufficiently wide and room temperature could be located near the middle of the hysteresis, then the alloy could be fabricated and

conveniently stored while in the martensitic condition. Since the hysteresis is sufficiently wide, the alloy would not transform to austenite until heated substantially above room temperature. This heating would not be applied until the alloy (in the form of a coupling, for example) was installed in its intended environment. The alloy, which would then be in the austenitic condition, would remain in the austenitic condition after cooling down since the service temperature (which may be above or below room temperature) would be substantially above the martensite transformation temperature. Thus, the above-noted desirable results could be achieved.

Unfortunately, there is believed to be no commercially viable nickel/titanium-based alloy that has a hysteresis sufficiently wide to achieve these desirable results.

For example, the commercially viable near equiatomic binary nickel-titanium alloys can have a hysteresis width of about 30°C. The location of the hysteresis for this alloy is also extremely composition sensitive so that while the hysteresis can be shifted from sub-zero temperatures to above-zero temperatures, the width of the hysteresis does not appreciably change. Thus, if the alloy were martensitic at room temperature, the service temperature must be above room temperature. Similarly, if the service temperature was at room temperature, the alloy would be martensitic below room temperature so that the alloy would require special cold-temperature equipment for fabrication, shipping, and storage. Ideally, as discussed above,

room temperature should be located near the middle of the transformation hysteresis. However, since the width of the hysteresis in the binary alloy is so narrow, the range of service temperatures for any particular alloy is necessarily limited. As a practical matter, the alloy would have to be changed to accommodate any change in service temperatures.

It can be appreciated that the relative lack of commercialization of shape memory alloys must be due, at least in part, to their extreme sensitivity to temperatures as discussed above. Alloying and processing have not solved the problem.

Nickel/titanium/iron alloys, e.g., those in Harrison et al., USP 3,753,700, while having a wide hysteresis, up to about 70°C, are the typical cryogenic alloys which always undergo the martensite/austenite transformation at sub-zero temperatures. It should be noted that in general, the colder shape-memory alloys such as the cryogenic alloys have a wider transformation hysteresis than the warmer shape memory alloys. In the case of the cryogenic alloys, the alloys must be kept very cold, usually in liquid nitrogen, to avoid the transformation from martensite to austenite. This makes the use of shape memory alloys inconvenient, if not uneconomical.

The nickel/titanium/copper alloys of Harrison et al., U.S. Patent Application No. 537,316, filed September 28, 1983, and the nickel/titanium/vanadium alloys of Quin, U.S. Patent Application Serial No. 541,844, filed October 14, 1983, are not cryogenic but

their hysteresis may be extremely narrow (10-20°C) such that their utility is limited for couplings and similar articles.

The problems experienced with the nickel/titanium-based shape memory alloys have been somewhat overcome by processing in the copper-based shape memory alloys. It is now known that the hysteresis in copper-based shape memory alloys can be temporarily expanded by mechanical preconditioning, austenitic aging and heat treating. In this regard, see Brook et al., USP 4,036,669; 4,067,752; and 4,095,999.

The methods of the Brook et al. patents have been applied to nickel/titanium-based alloys; however, it has been found that these methods have no beneficial effect on nickel/titanium-based alloys.

It is known that under certain conditions the hysteresis of nickel/titanium-based alloys can be shifted as opposed to expanded. It should be understood that shifting of the hysteresis means that the M_s, M_f, A_s, and A_f temperatures have all been translated to M_s', M_f', A_s' and A_f' such that there is substantially no change in the width of the hysteresis. It should be noted that the translated transformation temperatures may be higher or lower than the normal transformation temperatures. On the other hand, expansion of the hysteresis should generally be understood to mean that A_s and A_f have been elevated to A_s' and A_f' while at least M_s and usually also M_f remain essentially constant. Aging, heat treatment,

composition, and cold work can all effectively shift
the hysteresis. For example, if the stress is applied
to the shape memory alloy at room temperature the
hysteresis may be shifted so that the martensite phase
5   can exist at a temperature at which there would
normally be austenite. Upon removal of the stress, the
alloy would isothermally (or nearly isothermally)
transform from martensite to austenite.

10   Miyazaki et al., ("Transfomation Pseudoelasticity
and Deformation Behavior in a Ti-50.6 at % Ni Alloy",
Scripta Metallurgica, vol. 15, no. 3, pp. 287-292,
(1981) have studied the deformation behavior of binary
nickel-titanium alloys. As implied in Figure 3 of this
15   reference, the austenite transformation temperatures
can be elevated when nonrecoverable strain is imparted
to the alloy. That is, when the alloy was strained to
8% or higher and the stress then removed, there was
some component of the strain which remained at the
20   deformation temperature of 243°K (compared to an A_f of
221°K). This component recovered when heated to 373°K
(see dotted lines on Figure 3) although the precise
recovery temperature was never measured. It is not
clear from this reference whether the hysteresis was
25   shifted or expanded since the binary nickel-rich alloy
tested is extremely unstable when rapidly quenched as
was done in this reference. In fact, one skilled in
the art would have concluded that the hysteresis was
shifted and not expanded due to the unstable alloy
30   tested. There is no illustration of the transformation
hysteresis to contradict this conclusion.

In the Melton et al. patent previously mentioned, a

nickel/titanium/copper alloy was deformed beyond a
critical strain so as to impart nonrecoverable strain.
However, no expansion of the transformation hysteresis
was observed.

5

While it can be appreciated that it would be
desirable to have a nickel/titanium-based shape memory
alloy and article with a sufficiently wide
transformation hysteresis, the prior art has thus far
10 remained silent on a way to achieve it.

As mentioned earlier, shape-memory alloys have
found use in pipe couplings. The pipe coupling may be
a monolithic pipe coupling as described in the
15 earlier-mentioned Harrison and Jervis patents.
Alternatively, the pipe coupling may be a composite
coupling as described in the earlier-mentioned Clabburn
patent and in U.S. Patent Nos. 4,379,575; 4,455,041;
and 4,469,357 to Martin, the disclosures of which are
20 incorporated herein by reference. As noted in Martin,
the composite coupling comprises a driver member and a
sleeve member.

Composite couplings present the problem of how best
25 to assemble them. In the Martin patents, there are
noted several ways to assemble the couplings. In one
way, the sleeve may be assembled with the driver just
after the expansion of the driver so as to take
advantage of the elastic springback of the material.
30 The driver and sleeve membres are then stored in a
cryogenic fluid until ready for installation.

Alternatively, the driver alone may be stored in a
cryogenic fluid and then joined with the sleeve a the

time of installation. Once joined with the sleeve, the
driver is allowed to fully recover.

In practice, the driver may be expanded and, after
springback has occurred, joined with the sleeve while
both are immersed in a cryogenic fluid. Since no
recovery of the driver has occurred, the sleeve is only
loosely joined and would, in fact, become separated
from the driver if means were not provided to prevent
this separation. The means to prevent this separation
is usually provded in the form of a flaring of one end
of the sleeve which makes for a slight interference fit
between the sleeve and the driver.

All of these methods suffer from the disadvantage
that the driver must be stored in a cryogenic or other
cold fluid prior to installation. The second method
suffers from the additional disadvantage that the
driver may recover prior to joining with the sleeve,
thus rendering useless the composite coupling. The
last method disadvantageously required the additional
step of flaring the sleeve to prevent diengagement of
the driver and sleeve.

In Clabburn, a keeper is utilized to apply a stress
sufficient to temporarily raise the austenite
transformation temperature. The shape-memory alloy
remains in the martensitic state while the stress is
applied. This method is known as constrained storage.

It can be appreciated that it would be desirable to
have the driver and sleeve preassembled such that one
could merely remove the preassembled coupling from a

carton on a shelf and then proceed to install the
coupling without the need to worry about cold storage
of the coupling. Thus far, the prior art has remained
silent on a way to achieve this desirable result.

5

Thus, it is an object of the invention to have a
nickel/titanium-based shape memory alloy and article
with a wide transformation hysteresis.

10

It is another object of the invention to process a
nickel/titanium-based shape memory alloy and article so
as to temporarily enlarge the transformation hysteresis
of the alloy and article.

15

It is also an object of the invention to have a
method of preassembling a composite coupling without
the need for a cryogenic or other cold fluid.

It is another object of the invention to have a
20 method of preassembling a composite coupling wherein
the preassembled coupling may be stored without the
need for a cryogenic or othe cold fluid.

It is a further object of the invention to have a
25 composite coupling preassembled by the method of the
invention so that cryogenic or other cold fluid is not
necessary.

This invention relates to a method of processing a
30 nickel/titanium-based shape memory alloy. The purpose
of the method is temporarily to raise the A_s and A_f
temperatures to A_s' and A_f', respectively. This
method has been found useful in fabricating shape
memory alloy articles such as couplings.

There is also disclosed a method of preassembling a composite coupling. The coupling has at least one heat recoverable driver member and at least one metallic insert. The driver member is made from a

5   nickel/titanium-based shape memory alloy having a transformation hysteresis defined by M_s, M_f, A_s, and A_f temperatures. The method comprises overdeforming the driver member by applying a stress sufficient to cause nonrecoverable strain in the driver member so that the

10   A_s and A_f temperatures are temporarily raised to A_s, and $A_{f'}$, respectively; removing the stress; engaging the driver member and insert; and warming the driver and insert to a temperature less than A_s'.

15   We have found that by taking advantage of the expansion of the hysteresis caused by overdeformation of the driver member the composite coupling may be preassembled simply and efficiently.

20   Embodiments of the invention will now be described, by way of example, with reference to the accompanying drawings, wherein:

Figure 1 is a schematical illustration of the

25   shifting of the shape memory alloy transformation hysteresis.

Figure 2 is a schematical illustration of the expansion of the shape memory alloy transformation

30   hysteresis according to the invention.

Figure 3 is a schematical stress/strain curve for a binary nickel/ titanium-based shape memory alloy.

Figure 4 schematically illustrates the binary alloy strained as in Figure 3 in the unrecovered and recovered state.

Figure 5 is a schematical transformation hysteresis curve for a nickel/titanium/vanadium alloy after recovery of a 5% deformation and illustrating the presence of the R phase.

Figure 6 is a schematical transformation hysteresis curve for a nickel/titanium/vanadium alloy after recovery of a 16% deformation and illustrating the absence of the R phase.

Figure 7 is a schematical stress/strain curve similar to Figure 3 but for a typical nickel/titanium-based shape memry alloy.

Figure 8 schematically illustrates similar to Figure 3 the shape memory alloy strained in Figure 7 in the unrecovered and recovered state.

Referring to the figures in more detail and particularly referring to Figures 1 and 2, there is graphically illustrated the transformation hysteresis for a shape memory alloy. Figure 1 illustrates the shifting of the transformation hysteresis as would occur if, for example, a stress was applied. The hysteresis has moved upwardly in temperature from position 2 to position 4, shown in dotted lines. While the entire hysteresis has moved upwardly in temperature it can be seen that the width of the hysteresis, indicated generally by 6 has remained approximately

constant. In other words, M_s, M_f, A_s, and A_f have all been translated to higher temperatures and are now denoted as M_s', M_f', A_s', and A_f'. Of course, as stated earlier, there are circumstances where the transformation temperatures may be translated to lower temperatures.

In contrast to the shifting of the hysteresis as illustrated in Figure 1, Figure 2 now illustrates in general the expansion of the hysteresis. It can be seen that the martensite transformation temperatures remain constant but the austenite transition temperatures have been translated upwardly so that the width of the hysteresis indicated generally by 6 has now been expanded as indicated generally by 8. That is, M_s and M_f remain constant or nearly constant while A_s and A_f have been translated to higher temperatures and are now denoted as A_s' and A_f'.

The advantages of temporarily expanding the hysteresis versus shifting the hysteresis can be explained as follows. Referring again to Figure 1, a coupling may be expanded and held in the expanded condition so as temporarily to raise, i.e., temporarily shift, the hysteresis. As long as the stress is applied, the hysteresis will be shifted. If it is desired, for example, to use this coupling in ambient temperature, indicated by T_A, the coupling will not transform to austenite as long as temperature T_A is below A_s'. Upon the removal of the stress, the coupling will isothermally (or nearly isothermally) transform into austenite. In other words, the coupling will be at T_A when the stress is removed but the

hysteresis will have shifted from position 4 back to position 2. The coupling being martensitic before the shift from position 4 to position 2 must necessarily be austenitic after the shift. This method may be used
5 for constrained storage (see, e.g., Clabburn, USP 4,149,911) wherein a coupling is expanded and then held on a mandrel in the expanded condition until it is ready to be used, at which time it is cooled to below the M_s temperature so that it may be released from the
10 mandrel and then installed. The problem with this method is that while the coupling is held (during shipping, for example) in the expanded position which is necessary to shift the hysteresis, the coupling may relax so that a certain, perhaps very substantial,
15 amount of recovery motion will be permanently lost.

Referring now to Figure 2 it can be seen that by temporarily widening the hysteresis, as long as the coupling is held at a T_A less than A_s' there will be no
20 transformation. Since no stress need be continually applied to the coupling to widen the hysteresis, relaxation is not a problem. Upon use, the coupling would simply be heated above A_s', transformation from the martensite to the austenite would occur, and the
25 hysteresis would then shrink back down to its former position.

According to the invention there is disclosed a method of processing a nickel/titanium-based shape
30 memory alloy having a transformation hysteresis defined by M_s, M_f, A_s, and A_f temperatures. In general, the method comprises temporarily expanding the transformation hysteresis by elevating the A_s and A_f

temperatures to A_s' and A_f', respectively, so that the temperature difference between A_s' and M_s is greater than the temperature difference between A_s and M_s. The means for expanding the transformation hysteresis may be removed and then the alloy is stored at a temperature less than A_s'.

Usually, according to the invention, both the M_s and M_f temperatures will remain essentially constant during the expansion of the hysteresis. However, in certain alloys, as will become apparent hereafter, either or both of the M_s and M_f temperatures may permanently change. This change may result from the varying of the slope or even movement of the martensitic part of the transformation hysteresis curve due to the interaction of certain metallurgical conditions. However, the important point to emphasize here is that there will always be a net increase of the width of the transformation hysteresis according to the method of the invention.

The means for expanding the transformation hysteresis comprises overdeforming the alloy by applying a stress sufficient to cause nonrecoverable strain in the alloy. It should be understood that nonrecoverable strain means strain which is not recovered after deformation and subsequent no-load heating to at least the A_f' temperature.

It is important to understand and appreciate that the current practice in forming shape memory alloys as is well known to one skilled in the art is to void any nonrecoverable strain. The reason for avoiding any

nonrecoverable strain is that the presence of
nonrecoverable strain tends to reduce the amount of
motion upon recovery. It has been found, however, that
the amount of lost motion is relatively small when
compared to the enhanced utility of shape memory alloys
having an expanded transformation hysteresis according
to the present invention.

It is preferred that a stress is applied sufficient
to cause at least 1% or more of nonrecoverable strain
in the alloy. Usually (but not necessarily) after the
alloy is overdeformed the stress will be removed.

It is necessary to the invention that the
overdeforming takes place at a temperature which is
less than about the maximum temperature at which
martensite can be stress-induced. To those skilled in
the art this temperature is commonly known as M_d. It
is preferred however that the overdeforming temperature
be above M_s.

Once the hysteresis has been expanded at least
partial recovery of the alloy article can occur when
the alloy is heated to a temperature greater than about
A_s'. By heating to at least A_s' the transformation of
the martensite to the austenite can effectively begin.
It is preferred however that the heating temperature be
greater than A_f' so as to effect full recovery of the
alloy.

It has been found that the nickel/titanium-based
shape memory alloy may be a binary or it can be at
least a ternary. If it is a ternary

nickel/titanium-based shape memory alloy the ternary consists essentially of nickel, titanium and at least one other element selected from the group consisting of iron, cobalt, vanadium, aluminum, and niobium. The most preferred ternary, for reasons which will become apparent hereafter, consists essentially of nickel, titanium, and niobium.

It has also been found that those shape memory alloys having an M_s less than about 0°C are preferred since these alloys have the most utility and best performance.

The benefits of expansion of the shape memory alloy transformation hysteresis have already been disclosed in our U.S. Patent Application Serial No. 668,771 filed November 6, 1984 entitled "A Method of Processing a Nickel/Titanium-Based Shape Memory Alloy and Article Produced Therefrom" the disclosure of which is incorporated herein by reference. We have found that if in conjunction with the expansion of the hysteresis of the the driver member, the driver member is preassembled with the sleeve, then the preassembly is greatly facilitated.

Referring again to the figures Figure 7 schematically illustrates a stress-strain curve for a typical shape memory alloy which was overdeformed. The load was then removed. With overdeformation there is by definition a substantial amount of non-recoverable strain imparted to the alloy. Nonrecoverable strain will occur when the alloy, generally speaking, is strained past its second yield point indicated

approximately by reference numerical 10. After removal
of the stress, the alloy was heated.

In Figure 8 curve 12 illustrates the heating after
the removal of the stress. When the transformation was
complete the alloy was cooled down as illustrated by
curve 14. During the cooling down under a small load
and M_s and M_f temperatures were measured. The alloy
was then reheated (curve 16) to measure the recovered
austenitic transition temperatures A_s and A_f.

As we stated in our patent application above there
is more than one way to locate on a transformation
hysteresis curve the martensitic and austenitic
transformation temperatures. Referring again to figure
8 the literal starting and ending of the austenitic
transformation may be indicated for example by points
18 and 20 respectively on curve 12. However, the
austenitic transformation effectively begins at about
point 24 (denoted as A_s') and the austenitic
transformation effectively ends at about point 26
(denoted as A_f'). Thus it can be said that the bulk of
the transformation occurs between A_s' and A_f'. The
same is true for the other transformations as
illustrated by curves 14 and 16. The effective
austenitic and martensitic transformation temperatures
may be conveniently determined by the intersection of
tangents to the transformation hysteresis curves. For
example, tangents 22 on curve 12 locate A_s' and A_f'.

Whenever the austenitic and martensitic
transformation temperatures are mentioned in this
specification it should be understood that these

temperatures refer to the austentic and martensitic transformation temperatures determined by the above noted method of intersecting tangents. Whenever the literal starting and ending points of the martensitic and austentic transformations are indicated these temperatures will be referred to as the true martensitic and austenitic transformation temperatures. Thus, the literal starting and ending points of the austenitic transformation after expansion of the hysteresis are referred to as true A_s' and true A_f'.

Curves 14 and 16 represent the shape memory alloy transformation hysteresis in the recovered state while curves 12 and 14 represent the shape memory alloy transformation hysteresis in the unrecovered state. Thus it can be seen that the overdeformation of the alloy according to the patent application above has substantially and temporarily widened the hysteresis.

Now according to a second aspect of the invention there is disclosed a method of preassembling a composite coupling having at least one heat recoverable driver member and at least one metallic insert. The driver member is made from a nickel/titanium-based shape memory alloy having a transformation hysteresis defined by M_s, M_f, A_s and A_f temperatures. The method comprises overdeforming the driver member by applying a stress sufficient to cause nonrecoverable strain in the driver member so that the A_s and A_f temperature are temporarily raised to A_s' and A_f', respectively. The method further comprises removing the stress; engaging the driver member and insert; and then warming the driver and insert to a temperature less than A_s'.

Usually, as stated earlier, both the M_S and M_f temperatures will remain essentially constant during the expansion of the hysteresis. However, in certain alloys either or both of the M_S and M_f temperatures may
5   permanently change. This change may result from the varying of the slope or even movement of the martensitic part of the transformation hysteresis curve due to the interaction of certain metallurgical conditions. However, the important point to emphasize
10   here is that there will always be a net increase of the width of the transformation hysteresis according to the method of the invention. That is, the temperature difference between A_S' and M_S will be greater than the temperature difference between A_S and M_S.

15

According to the invention, there must be at least one driver member; however, there may be more than one such as when ring drivers are used. Similarly, there must be at least one insert but there may be mroe than
20   one such as when mult-piece inserts were utilized.

It should be understood that while the driver and insert preferably need to be warmed to a temperature which is less than A_S', they in any case need to be
25   raised to a temperature above the true A_S'. The reason for this is that below true A_S' there will not be any recovery of the shape memory alloy. Referring again to figure 8 it can be seen that between true A_S' and A_S' there will be a small amount of recovery indicated by
30   28. After A_S' is passed the bulk of the recovery will effectively occur as indicated by 30. From figure 8 then it is apparent that to get to any amount of recovery the material has to be heated above true A_S'.

However, since the amount of recovery occurring between true A_s' and A_s' is much less than the recovery occurring between A_s' and true A_f' little shape memory recovery will actually be lost by allowing the driver member to partially recover according to the invention. This partial recovery is not so great as to crush the insert but only so great as to be able to hold the insert and driver snugly engaged.

It should be understood that the metallic insert may take many forms. for example, the insert may be tubular, tapered or slotted, all of which are disclosed in the above Martin patents. Additionally, the insert may be single or multipiece. Finally, the insert may have an irregular shape such as to be x-shaped, y-shaped or t-shaped.

The insert may also have sealing means as also disclosed in the above Martin patents. The sealing means any comprise, for example, teeth or gall-prone materials.

It should also be understood that the driver member may take many forms. It is preferred, however, that the driver member be a tubular driver or a ring driver.

In the step of overdeforming the driver member it is preferred that a stress is applied sufficient to cause at least one percent of nonrecoverable strain in the driver member. Of course the nonrecoverable strain may be much more than one percent which is usually the case but it is preferred that there be at least one percent strain.

It is preferred that the overdeforming take place
at a temperature which is less than about the maximum
temperature at which martensite can be stress-induced.
The temperature is also known as the M_d temperature.
The reason for this is that when the material has been
deformed at a termperature greater than M_d the amound
of strain recoverable upon subsequent heating is
drastically and dramatically reduced. Generally, the
more the deformation temperature is raised above M_d,
the greater will be the reduction in recoverable
strain. It is most preferred that the overdeforming
temperature be between M_s and A_s.

It is desirable that the nickel/titanium-based
shape memory alloy has an M_s temperature less than
about 0°C. However, it is preferred that the
nickel/titanium-based shape memory alloy is stable,
does not contain an R phase and has an M_s temperature
less than about 0°C. To those skilled in the art the R
phase is known as a transitional phase between the
austentite and martensite and has a structure different
than either. The effect of the R phase is to depress
the austenitic and martensitic transformation
temperatures. Alloys that are stable (i.e. exhibit
temper stability) have an M_s that does not change more
than about 20°C after annealing and water quenching and
subsequent aging between 300 and 500°C.

The nickel/titanium-based shape memory alloy may be
a binary or at least a ternary. In the case where the
shape memory alloy is a ternary, the ternary may
comprise nickel/titanium and at least one other element
selected from the group consisting of iron, cobalt,

vanadium, aluminum and niobium. It is most preferred
that the ternary nickel/titanium-based shape memory
alloy comprise nickel, titanium and niobium.

5   It is believed that the teaching of this invention
will have most application to couplings processed by
the method of the invention. However it should be
understood that the teaching of the invention applies
to other articles and devices processed by the method
10   of the invention.

        Embodiments of the invention are now described, by
way of example, with reference to the following
examples.

15

Example 1

        Commercially pure titanium and carbonyl nickel were
weighed in proportions so as to give a composition of
20   50.7 atomic percent nickel and 49.3 atomic percent
titanium. The total mass for test ingots was about 330
grams. These metals were placed in a water-cooled,
copper hearth in the chamber of an electron beam
melting furnace. The chamber was evacuated to 10^{-5}
25   Torr and the charges were melted and alloyed by use of
the electron beam.

        The resulting ingots were hot swaged and hot rolled
in air at approximately 850°C to produce a strip of
30   approximately 0.025-in. thickness. Samples were cut
from the strip, descaled and vacuum annealed at 850°C
for 30 minutes and furnace cooled. The strip was then
elongated. After elongation the stress was removed and

the strip was heated unrestrained so as to effect
recovery of the shape memory alloy. The recovery was
monitored and plotted as a function of temperature.
When the transformation was complete, the sample was
5   cooled and then reheated so as to complete the
measurement of the martensite and austenite
transformation temperatures before recovery and after
recovery. The results are tabulated below in Table 1.

10   The measure A_S' minus M_S is very useful since M_S is
directly indicative of the lower functional limit of
the alloy and the A_S' is directly indicative of the
highest temperature which may be encountered (e.g.
during storing and shipping) before the austenite
15   transformation will effectively begin. Thus, A_S' minus
M_S defines the operating range of the alloy when
processed according to the invention. This measure
should be compared to A_S minus M_S which defines the
operating range of the alloy after the temporary
expansion of the hysteresis has been recovered. As
20   minus M_S is also indicative of the operating range of
the alloy if it were never processed according to the
invention. Thus, comparing A_S' minus M_S to A_S minus M_S
provides useful indicia of the expansion of the
hysteresis as well as the advantages of the invention.
25

Referring now to Table 1, A_S' minus M_S and A_S minus
M_S are about the same at 5% elongation; however, at 16%
elongation, the difference becomes substantial. It is
30   useful to note that A_S' after 16% elongation is above
normal room temperature so that the alloy may now be
handled at room temperature so that the alloy may now
be hadled at room temperature without the necessity of
providing a cold environment.

Another useful measurement for indicating the
expansion of the hysteresis are the M_{50}, A_{50}, and A_{50}'
values. These are the martensite and austenite
transformation temperatures at which the transformation
is 50% complete. Thus, referring to Table 1 it can be
seen that the the sample was cooled and then reheated
so as to complete the measurement of the martensite and
austenite transformation temperatures before recovery
and after recovery. The results are tabulated below in
Table 1.

The measure A_S' minus M_S is very useful since M_S is
directly indicative of the lower functional limit of
the alloy and the A_S' is directly indicative of the
highest temperature which may be encountered (e.g.
during storing and shipping) before the austenite
transformation will effectively begin. Thus, A_S' minus
M_S defines the operating range of the alloy when
processed according to the invention. This measure
should be compared to A_S minus M_S which defines the
operating range of the alloy after the temporary
expansion of the hysteresis has been recovered. As
minus M_S is also indicative of the operating range of
the alloy if it were never processed according to the
invention. Thus, comparing A_S' minus M_S to A_S minus M_S
provides useful indicia of the expansion of the
hysteresis as well as the advantages of the invention.

Referring now to Table 1, A_S' minus M_S and A_S minus
M_S are about the same at 5% elongation; however, at 16%
elongation, the difference becomes substantial. It is
useful to note that A_S' after 16% elongation is above
normal room temperature so that the alloy may now be

handled at room temperature so that the alloy may now
be hadled at room temperature without the necessity of
providing a cold environment.

Another useful measurement for indicating the
expansion of the hysteresis are the M_{50}, A_{50}, and A_{50}'
values. These are the martensite and austenite
transformation temperatures at which the transformation
is 50% complete.

Table 1

| | | | Nickel/Titanium Binary (50.7/49.3) | |
| | | | % Elongation[*] | |
			5	16
A_S',	°C		5	32
A_{50}',	°C		12	39
A_f',	°C		16	50
M_S,	°C		-32	-30
M_{50},	°C		-52	-52
M_f,	°C		-71	-80
A_S,	°C		0	-15
A_{50},	°C		8	8
A_f,	°C		13	32
A_{50}' − M_{50},	°C		64	91
A_{50} − M_{50},	°C		60	60
A_S' − M_S			37	62
A_S − M_S			32	15

[*]elongated at -50°C

In referring to Table 1 it can be seen that the
difference between M_{50} and A_{50}, the permanent width of
the hysteresis, is about 60°C. However, the width of
the hysteresis may be temporarily enlarged, i.e., A_{50}'

minus M_{50}, from 64°C at 5% elongation (at which there is no nonrecoverable strain) to 91°C at 16% elongation (at which there is substantial nonrecoverable strain). The M_{50}, A_{50}, and A_{50}' values are also useful because they are the most easily determined as will become apparent hereafter.

These results are graphically illustrated in Figures 3 and 4. Figure 3 illustrates a stress/strain curve for the binary alloy which was strained to 16%. The load was then removed. With 16% strain there is a substantial amount of nonrecoverable strain imparted to the alloy. Nonrecoverable strain will occur when the alloy, generally speaking, is strained past its second yield point indicated approximately by reference numeral 10. After removal of the stress, the alloy was heated.

In Figure 4, curve 12 illustrates the heating after the removal of the stress. When the transformation was complete, the alloy was cooled down as illustrated by curve 14. During the cooling down under a small load the M_S and M_f temperatures were measured. The alloy was then reheated (curve 16) to measure the recovered austenite transition temperatures A_S and A_f.

There is more than one way to locate on a transformation hysteresis curve the martensite and austenite transformation temperatures. Referring again to Figure 4, the literal starting and ending of the austenite transformation may be indicated, for example, by points 18 and 20, formation effectively begins at about point 24 (denoted as A_S') and the austenite

transformation effectively ends at about point 26
(denoted as A_f'). Thus it can be said that the bulk of
the transformation occurs between A_s' and A_f'. The
same is true for the other transformations as
5   illustrated by curves 14 and 16. The effective
austenite and martensite transformation temperatures
may be conveniently determined by the intersection of
tangents to the transformation hysteresis curves. For
example, tangents 22 on curve 12 locate A_s' and A_f'.
10   The mid-point of the transformation, for example A_{50}'
on curve 12, is simply vertically equidistant from the
literal starting and ending points, for example 18 and
20 on curve 12, of the transformation.

15   Whenever the austenite and martensite
transformation temperatures are mentioned in this
specification, it should be understood that these
temperatures refer to the austenite and martensite
transformation temperatures determined by the
20   above-noted method of intersecting tangents.

Curves 14 and 16 represent the shape memory alloy
transformation hysteresis in the recovered state while
curves 12 and 14 represent the shape memory alloy
25   transformation hysteresis in the unrecovered state.
Thus it can be seen that the elongation of the alloy
according to the invention has substantially and
temporarily widened the hysteresis.

30   In sum, the expansion of the hysteresis will
facilitate the convenient handling and shipping of the
alloy. This particular binary alloy would now be more
suitable for a variety of applications and temperatures

where the service temperature is above room temperature.

Example 2

Commercially pure titanium, carbonyl nickel and iron were weighed in proportions so as to give a composition of 47 atomic percent nickel, 50 atomic percent titanium and 3 atomic percent iron. The total mass for test ingots was about 330 grams. These alloys were melted in an electron beam furnace in the same manner as the nickel-titanium binary. The resulting ingots were hot swaged at approximately 850°C. Round, tensile bars (1/4" in diameter) were then machined from the hot swaged ingot, vacuum annealed at 850°C for 30 minutes, and then furnace cooled.

The tensile bars were then elongated. After elongation the stress was removed and the bars were heated so as to effect recovery of the ternary shape memory alloy in the same manner as the binary alloy. Due to the extreme low temperatures involved, some of the values had to be extrapolated as noted. The results are tabulated below in Table 2.

The discrepancy in the martensite and austenite transformation temperatures (between 5 and 16% elongation) can be explained in part by the interference of the R phase, to be discussed in more detail later.

As it can be appreciated, the width of the hysteresis and the operating range have been enlarged

as a result of the 16% elongation of the alloy. The import of this is that after elongation of the alloy, the alloy no longer has to be stored in liquid nitrogen to prevent it from transforming into austenite. Since A_S' has been raised to -88°C other forms of cold storage may now be used to store and ship the nickel/titanium/iron alloy prior to its final use. It is believed that this will result in greater utility of the alloy.

Table 2

Nickel/Titanium/Iron Ternary (47/50/3)		
	% Elongation*	
	5	16
A_S', °C	-127	- 88
A_{50}', °C	-124	- 77
A_f', °C	-122	- 66
M_S, °C[b]	-186 (-156)	-180 (-150)
M_{50}, °C[b]	-200 (-170)	-187 (-157)
M_f, °C[b]	a	-194 (-164)
A_S, °C[b]	-147 (-117)	-130 (-100)
A_{50}, °C[b]	-142 (-112)	-118 (- 88)
A_f, °C[b]	-132 (-102)	-104 (- 74)
A_{50}' - M_{50}, °C	76	110
A_{50} - M_{50}, °C	58	69
A_S' - M_S	59	92
A_S - M_S	39	50

*elongated in liquid nitrogen (-190°C)
[a]not measurable (below liquid nitrogen)
values are extrapolated to no load from
values measured at 20 ksi load in parentheses

Example 3

Commercially pure titanium, carbonyl nickel and niobium were weighed in proportions so as to give a composition of 47 atomic percent nickel, 44 atomic percent titanium, and 9 atomic percent niobium. The total mass for test ingots was about 330 grams. The composition was melted in an electron beam furnace as was the case with the alloys in Examples 1 and 2. The resulting ingots were hot swaged in air at approximately 850°C. The resulting bar was machined into rings which were vacuum annealed in 850°C for 30 minutes and then furnace cooled. The rings were then enlarged, unstressed and subsequently heated so as to measure the free recovery of the alloy. The results are tabulated below in Table 3.

Table 3

	Nickel/Titanium/Niobium Ternary (47/44/9)						
	% Enlargement						
	5.2[a]	12.1[a]	16.2[a]	16.2[b]	16.2[c]	16.0[d]	16.2[e]
A_S', °C	− 14	27	41	50	54	34	55
A_{50}', °C	− 6	29	45	53	58	50	58
A_f', °C	3	32	49	56	61	67	60
M_S, °C	− 90	− 90	− 90	− 90	− 90	− 90	− 90
M_{50}, °C	− 95	− 95	− 95	− 95	− 95	− 95	− 95
M_f, °C	−100	−100	−100	−100	−100	−100	−100
A_S, °C	− 56	− 56	− 56	− 56	− 56	− 56	− 56
A_{50}, °C	− 40	− 40	− 40	− 40	− 40	− 40	− 40
A_f, °C	− 27	− 27	− 27	− 27	− 27	− 27	− 27
$A_{50}'-M_{50}$, °C	89	124	140	148	153	145	153
$A_{50}-M_{50}$, °C	55	55	55	55	55	55	55
$A_S'-M_S$ °C	76	117	131	140	144	124	145
A_S-M_S, °C	34	34	34	34	34	34	34

[a]enlarged in liquid nitrogen (-196°C)
[b]enlarged in -90°C alcohol
[c]enlarged in -70°C alcohol
[d]enlarged at 0°C
[e]enlarged in -90°C alcohol; reenlarged at 20°C

It can be seen from Table 3 that the hysteresis width ($A_{50}-M_{50}$) in the fully recovered state is about 55°C with A_S being -56°C. With the austenite temperature in this range it is still necessary for the alloy to be cold stored in order to prevent transformation of the martensite into the austenite. However, if the ring is now enlarged about 5%, the A_S temperature has been temporarily raised to -14°C which would still require cold storage. By enlarging the ring 12.1% at which point there is now substantial nonrecoverable strain, the A_S has been temporarily

increased to 27°C. Thus, at this temperature the alloy
may be stored and shipped at room temperature. No cold
storage provisions are required. It also can be seen
that the width of the hysteresis has now been increased
5   to 124°C from 55°C and the operating range $(A_S'-M_S)$ has
been increased to 117°C. By enlarging the ring 16.2%
A_S has now been temporarily raised to 41°C with the
width of the hysteresis now being 140° and the
operating range now being 131°C.

10

     It is believed that to have the most commercially
practical alloy it is necessary to have an hysteresis
width of greater than about 125°C with ambient or room
temperature somewhere in the middle of that hysteresis
15   so as to allow a substantial leeway on either side of
room temperature for temperature excursions. Strictly
speaking, it would be most preferred if the A_S' could
be raised to about 50°C.

20   The first three samples enlarged at 5.2, 12.1, and
16.2% were enlarged in liquid nitrogen which is
substantially below M_S. If the samples were now
enlarged in -90°C alcohol, which is at the M_S
temperature, it can be seen that the austenite
25   transition temperatures have been raised to higher
values than when enlarged in liquid nitrogen. By
comparison, the A_S' temperatures have been raised from
41 to 50°C. While this increase is not of great
magnitude it is nevertheless important.

30

     It is most preferred that the temperature of
deformation be above M_S. The importance of this
limitation is illustrated in the next sample which was

deformed at -70°C (compared to an M_s of -90°C). It can be seen that A_s', and $A_{50}'-M_{50}$ and $A_s'-M_s$ have all been increased more than any of the previous samples.

5   The next sample was enlarged at 0°C. While it can be seen that the hysteresis has been expanded, the effect of the expansion of the hysteresis has not been as great as when it was enlarged in -90°C alcohol or -70°C alcohol since A_s' has only been raised to 34°C.

10

     The previously stated results have been obtained by expanding the hysteresis through overdeforming of the alloy so as to impart nonrecoverable strain, removing the stress and then storing the alloy at a temperature

15 less than A_s'.

     The process may be varied somewhat so as to give equally dramatic results. Thus a sample may be overdeformed at low temperatures such as -90°C in

20 alcohol to stabilize the martensite at or near room temperature. When the stress is removed there will be an elastic springback of about 4%. Now if the alloy is redeformed at 20°C to the same amount of overdeformation, 16.2%, and the stress removed, it can

25 be seen in the last column of Table 3 that the austenite transition temperatures have been raised to even higher values when compared to a single expansion in -90°C alcohol. Thus, A_s' has been moved from 50°C to 55°C. Again, while this increase in A_s' may appear

30 to be a small amount of temperature increase it is nevertheless of great importance. One easy way to accomplish this process is to deform the ring on a mandrel and then let the ring and mandrel warm to room temperature.

The nickel/titanium/niobium ternary alloys are
preferred alloys due to their ready susceptibility to
expansion of the transformation hysteresis as
illustrated above. Of all the ternary niobium alloys,
those that are stable, have an M_s greater than 0°C and
do not have an R phase are the most preferred. The R
phase, as further discussed below, is a transitional
phase between austenite and martensite. Since the R
phase is not present, there is substantial uniformity
in the martensite and austenite transformation
temperatures from sample to sample. Alloys that are
stable (i.e., exhibit temper stability) have an M_s that
does not change more than about 20°C after annealing
and water quenching and subsequent aging between 300
and 500°C.

Examples 4, 5, and 6

Commercially pure titanium, carbonyl nickel and
amounts of vanadium, cobalt, and aluminum were weighed
in proportions so as to give compositions of: 46
atomic percent nickel, 49 atomic percent titanium, and
5 atomic percent vanadium; 49 atomic percent nickel, 49
atomic percent titanium, and 2 atomic percent cobalt;
and 50 atomic percent nickel, 48.5 atomic percent
titanium, and 1.5 atomic percent aluminum. Each of the
compositions was melted and 0.025-in.-thick strips
prepared in the same way as that previously stated with
respect to the binary.

After elongation, the stress was removed and the
strip was heated unrestrained so as to effect recovery
which was monitored and plotted as a function of

temperature. When the transformation was complete, the
sample was cooled and then reheated so as to complete
the measurement of the martensite and austenite
transformation temperatures before recovery and after
5 recovery. In the case of the cobalt alloy, the
martensite and austenite transformation temperatures
were measured with a load of 20 ksi and then
extrapolated to 0 ksi. The results are tabulated below
in Tables 4, 5, and 6.

10

Table 4

Nickel/Titanium/Vanadium Ternary (46/49/5)		
	% Elongation*	
	5	16
A_S', °C	-20	84
A_{50}', °C	-17	95
A_f', °C	-15	105
M_S, °C	-46	10
M_{50}, °C	-68	-17
M_f, °C	-96	-50
A_S, °C	-24	40
A_{50}, °C	-17	50
A_f, °C	-10	70
$A_{50}' - M_{50}$, °C	51	112
$A_{50} - M_{50}$, °C	51	67
$A_S' - M_S$, °C	26	74
$A_S - M_S$, °C	22	30

*elongated at -100°C

Referring to Table 4, the large discrepancy between
the martensite and austenite transformation

temperatures at 5 and 16%, respectively, is believed
due to the interference of the R-phase. Referring to
Figure 5, the presence of the R phase 28 is most
noticeable on the austenite leg of the transformation
hysteresis for the alloy deformed 5%. As stated
previously the R phase is a transitional phase between
the austenite and martensite and has a structure
different than either. The effect of the R phase is to
depress the austenite and martensite transformation
temperatures. Figure 6 illustrates the transformation
hysteresis curve for the same alloy, but after
recovering from 16% deformation. The R phase is
noticeably absent. The austenite and martensite
transformation temperatures in Figure 6 are also
noticeably higher.

Referring again to Table 4, it can be seen that a
5% deformation has little effect on the expansion of
the hysteresis. Thus, A_S' minus M_S and A_S minus M_S are
substantially the same. This is not the case after 16%
deformation wherein the transformation hysteresis has
been noticeably enlarged.

The results in Table 5 are similar to those in
Table 4 in that a 5% deformation (no nonrecoverable
strain) had little effect on the expansion of the
transformation hysteresis whereas a 16% deformation
(substantial nonrecoverable strain) had a marked effect
on the expansion of the transformation hysteresis.

The change in the recovered martensite and
austenite transformation temperatures between the 5%
and 16% deformations is again believed due to the
interference of the R phase in the sample deformed 5%.

Table 5

Nickel/Titanium/Cobalt Ternary (49/49/2)		
	% Elongation*	
	5	16
A_s', °C	− 81	− 54
A_{50}', °C	− 76	− 36
A_f', °C	− 71	− 18
M_s, °C[a]	−119	−145
M_{50}, °C[a]	−141	−160
M_f, °C[a]	−155	−175
A_s, °C[a]	− 85	−100
A_{50}, °C[a]	− 75	− 90
A_f, °C[a]	− 67	− 80
$A_{50}' - M_{50}$, °C	65	124
$A_{50} - M_{50}$, °C	66	70
$A_s' - M_s$, °C	38	91
$A_s - M_s$, °C	34	45

*elongated at −100°C
[a]extrapolated to 0 ksi load from 20 ksi load

Table 6

Nickel/Titanium/Aluminum Ternary (50/48.5/1.5)		
	% Elongation*	
	5	16
A_s', °C	− 16	20
A_{50}, °C	− 12	29
A_f', °C	− 6	42
M_s, °C	− 67	− 72
M_{50}, °C	− 84	−104
M_f, °C	−108	−122
A_s, °C	− 24	− 32
A_{50}, °C	− 12	− 20
A_f, °C	0	3
$A_{50}' - M_{50}$, °C	72	133
$A_{50} - M_{50}$, °C	72	84
$A_s' - M_s$, °C	51	92
$A_s - M_s$, °C	43	40

*elongated at −100°C

Referring now to Example 6 and Table 6, the sample deformed 16%, and thus having substantial nonrecoverable strain, shows a marked expansion of the transformation hysteresis (as in the previous two examples) whereas the sample deformed at 5% shows essentially no expansion of the transformation hysteresis.

Again, the interference of the R phase has manifested itself by depressing the martensite and austenite transformation temperatures in the sample deformed 5%.

It bears repeating here that the lack of utility of shape memory alloys has resulted at least in substantial part from the fact that the alloys cannot be deformed and then stored at room temperature. The present invention has solved all the problems of the prior art and has now resulted in an alloy and article which at least in the case of the most preferred niobium ternary alloy can be deformed and stored at room temperature or at least can be deformed in cold temperatures but can be stored and shipped at room temperature without the provision of cold storage procedures.

It can be appreciated that while this invention is most advantageous with respect to those alloys having an enlarged hysteresis with its middle near room temperature, it is within the scope of the invention to apply the teachings of this invention to other alloys as well, as illustrated in the above examples.

It can also be appreciated that the expansion of the transformation hysteresis will be more dramatic in some alloys than in others. This conclusion becomes apparent when comparing the transformation hysteresis expansion of the binary alloy with the transformation hysteresis expansion of the most preferred niobium ternary alloy.

Example 7

A cylindrical driver member was made from an alloy having the composition of 47 atomic percent nickel, 44 atomic percent itanium and 9 atomic percent niobium.

The nickel/titanium/niobium alloys, in general, are the
most preferred alloys. These alloys were described in
our U.S. Patent Application Serial No. 668,777 filed
November 6, 1984, entitled "Nickel/Titanium/Niobium
5   Shape Memory Alloy and Article", the disclosure of
which is incorporated by reference herein.

        The driver was melted and processed as noted in our
patent application above except that a coupling was
10   machined instead of a ring. The driver was machined to
have an inside diameter of .847 inches, an outside
diameter of 1.313 inches and a length of 2.12 inches.

        A cylindrical insert was then made to be eventually
15   joined with the driver so as to form a composite
coupling. The insert was machined from 316 stainless
steel so as to have an inside diameter of .850 inches,
an outside diameter of .970 inches and a length of 2.12
inches. It is not necessary to the invention that the
20   insert be made from stainless steel. It is only
necessary that the insert be made from a material that
is sufficiently soft such that it may be crushed by the
driver upon full recovery thereof.

25   With the particular alloy utilized, the M_S
temperature was -90°C, the A_S temperature was -56°C and
the M_d temperature was -10°C. Although not actually
measured, such an alloy expanded about 16% at -50°C
would be expected to have a true A_S' of -52°C and an
30   A_S' of +52°C. Thus, immediately after expansion, the
driver was near the literal starting temperature of the
austenitic transformation of the temporarily expanded
transformation hysteresis.

After expansion, the driver was removed from the cold fluid and placed on a work bench. The insert was then slipped into the driver. Thereafter, the driver and insert were allowed to warm to room temperature, which it is noted is substantially below A_s'. It was found that the driver and insert were snugly engaged and could only be moved relative to each other with great difficulty. It should be noted that while the driver and insert became snugly engaged, there was no crushing of the insert.

The driver, prepared as described above, would be expected to have about 8% recoverable strain. About 1% of that recoverable strain was utilized in the preassembling of the driver and insert. Thus, about 7% recoverable strain remains for the actual coupling of the substrates.

The composite coupling is now preassembled and ready for storage or use.

Example 8

Commercially pure titanium, carbonyl nickel and niobium were weighed in proportions so as to give a composition of 47 atomic percent nickel, 44 atomic percent titanium, and 9 atomic percent niobium. The total mass for test ingots was about 330 grams. These metals were placed in water-cooled, copper hearth in the chamber of an electron beam melting furnace. The chamber was evacuated to 10^{-5} Torr and the charges were melted and alloyed by use of the electron beam. The resulting ingots were hot swaged in air at

approximately 850°C. The resulting bar was machined into rings which were vacuum annealed in 850°C for 30 minutes and then furnace cooled. The rings were then enlarged, unstressed and subsequently heated so as to measure the free recovery of the alloy. The results are tabulated below in Table 7.

Table 7

Nickel/Titanium/Niobium Ternary (47/44/9)

Expansion Temperature, °C

	-196	-90	-70	-30	-10	-0
True A_S', °C	-62	-56	-25	-67	-60	-50
A_S', °C	43	52	54	53	44	34
M_S, °C	-90	-90	-90	-90	-90	-90
A_S, °C	-56	-56	-56	-56	-56	-56
M_d, °C	-10	-10	-10	-10	-10	-10

While the data relate to the expansion of rings, the date is nevertheless indicative of how the material would perform as a driver. In each case, there is a substantial difference between true A_S' and A_S' indicating that the material will achieve the objects of the invention. The true A_S' for the sample expanded at -70°C is believed to be an anomaly in that the sample may have inadvertently warmed to near room temperature prior to the actual measurement of true A_S' and A_S'.

It is preferred that the material be expanded at temperatures no higher than M_d (-10°C in Table 1) since expansion at higher temperatures will cause a dramatic decrease in the amount of recoverable strain obtainable. However, expansion at temperatures higher

than M_d does not appear to affect the difference between true A_S' and A_S'.

It is most preferred that expansion takes place between A_S and M_S. This is because at temperatures higher than A_S or lower than M_S, elastic springback of the material may be increased. Additionally, the material has somewhat more ductility when expanded between A_S and M_S.

Examples 9 to 13

Commercially pure titanium and carbonyl nickel were weighed in proportions so as to give a composition of 50.7 atomic percent nickel and 49.3 atomic percent titanium. Additionally, commercially pure titanium, carbonyl nickel and amounts of vanadium, cobalt, aluminum and iron were weighed in proportions so as to give compositions of: 46 atomic percent nickel, 49 atomic percent titanium and 5 atomic percent vanadium; 49 atomic percent nickel, 49 atomic percent titanium and 2 atomic percent cobalt; 50 atomic percent nickel, 48.5 atomic percent titanium and 1.5 atomic percent aluminum; and 47 atomic percent nickel, 50 atomic percent titanium and 3 percent iron.

These metals were placed in a water-cooled, copper hearth in the chamber of an electron beam melting furnace. The chamber was evacuated to 10^{-5} Torr and the charges were melted and alloyed by use of the electron beam.

The resulting iron-containing ingots were hot swaged at approximately 850°C. Round, tensile bars ($\frac{1}{4}$"

in diameter) were then machined from the hot swaged
ingot, vacuum annealed at 850°C for 30 minutes, and
then furnace cooled. The tensile bars were then
elongated. After elongation, the stress was removed
and the bars were heated unrestrained so as to effect
recovery of the shape memory alloy. The recovery was
monitored and plotted as a function of temperature.
When the transformation was complete, the sample was
cooled and then reheated so as to complete the
measurement of the martensitic and austenitic
transformation temperatures before recovery and after
recovery. The results are tabulated in Table 8.

The remaining ingots were hot swaged and hot rolled
in air at approximately 850°C to produce a strip of
approximately 0.025-in. thickness. Samples were cut
from the strip, descaled and vacuum annealed at 850°C
for 30 minutes and furnace cooled. The stip was then
elongated. After elongation, the stress was removed
and the strip was heated unrestrained so as to effect
recovery which was monitored and plotted as a function
of temperature. When the transformation was complete,
the sample was cooled and then reheated so as to
complete the measurement of the martensitic and
austenitic transformation temperatures before recovery
and after recovery. In the case of the cobalt alloy,
the martensitic and austenitic transformation
temperatures were measured with a load of 20 ksi and
then extrapolated to 0 ksi. The results are tabulated
below in Tables 9 to 12.

Table 8

Nickel/Titanium/Iron Ternary (47/50/3)

	Expansion Temperature $-196°C$
True A_S', °C	< -196
A_S', °C	-90
M_S, °C	-154
A_S, °C	-137

Table 9

Nickel/Titanium Binary (50.7/49.3)

	Expansion Temperature $-50°C$
True A_S', °C	-55
A_S', °C	32
M_S', °C	-30
A_S, °C	-15

Table 10

Nickel/Titanium/Vanadium Ternary (46/49/5)

	Expansion Temperature $-100°C$
True A_S', °C	20
A_S', °C	84
M_S, °C	10
A_S, °C	40

Table 11

Nickel/Titanium Cobalt Ternary (49/49/2)

	Expansion Temperature -100°C
True A_S',°C	-100
A_S',°C	-54
M_S',°C	-154
A_S,°C	-100

Table 12

Nickel/Titanium/Aluminum (50/48.5/1.5)

	Expansion Temperature -100°C
True A_S',°C	-24
A_S',°C	20
M_S,°C	-72
A_S,°C	-32

As stated earlier it is believed that the above data while not derived from drivers per se is nevertheless indicative of how each of these materials will perform as a driver. Thus, for each of these materials, in addition to having an expanded hysteresis, there is a substantial difference between A_S' and A_S' so that these materials are suitable to achieve the objects of the invention.

Finally, it can be apprecated that while the samples in the above examples were deformed by application of a tensile stress, the objects of the invention can be fully achieved by application of a compressive stress.

The invention, as defined by the claims provides a
number of methods. Articles by any one, or any
combination of those methods also form part of the
present invention. Particularly preferred articles
5   include couplings.

CLAIMS:

1. A method of processing a nickel/titanium-based shape memory alloy having a transformation hysteresis defined by M_S, M_f, A_S, and A_f temperatures, the method comprising:

temporarily expanding the transformation hysteresis by elevating the A_S and A_f temperatures to A_S' and A_f', respectively, so that the temperature difference between A_S' and M_S is greater than the temperature difference between A_S and M_S; and

storing the alloy at a temperature between A_S and A_S'.

2. A method according to Claim 1 wherein the step of expanding the transformation hysteresis comprises overdeforming the alloy by applying a stress sufficient to cause nonrecoverable strain in the alloy.

3. A method of processing a nickel/titanium-based shape memory alloy having a transformation hysteresis defined by M_S, M_f, A_S, and A_f temperatures, the method comprising:.

overdeforming the alloy by applying a stress sufficient to cause nonrecoverable strain in the alloy wherein the transformation hysteresis is temporarily expanded by elevating the A_S and A_f temperatures to A_S' and A_f', respectively, so that the temperature difference between A_S' and M_S is

greater than the temperature difference between A_s and M_s.

4. A method of Claim 3 further comprising the step of storing the alloy at a temperature less than about A_s'.

5. A method according to Claim 2, 3 or 4, further comprising the step of removing the stress.

6. A method of preassembling a composite coupling having at least one heat-recoverable driver member and at least one metallic insert, the driver member made from nickel/titanium-based shape memory alloy having a transformation hysteresis defined by M_s, M_f, A_s, and A_f temperatures, the method comprising:

overdeforming the driver member by applying stress sufficient to cause nonrecoverable strain in the driver member so that the A_s and A_f temperatures are temporarily raised to A_s' and A_f', respectively; removing the stress; engaging the driver member and insert; and warming the driver member and insert to a temperature less than A_s'.

7. A method according to any preceding Claim wherein in overdeforming the alloy or the driver member, a stress is applied sufficient to cause at least one percent of nonrecoverable strain in the alloy.

8. A method according to any preceding Claim wherein the overdeforming takes place (a) at a temperature that is less than about the maximum temperature at which martensite can be stress induced, and/or

(b) at a temperature that is greater than M_S, and
is preferably at a temperature between M_S and A_S.

9. A method according to any preceding Claim wherein
the overdeforming takes place at a first temperature,
the method further comprising the step of raising
the temperature of the alloy or driver member to a
second temperature, which is preferably room
temperature, while maintaining the applied strain.

10. A method according to Claim 5, or any Claim
dependant theron, wherein the overdeforming takes place
at a first temperature and further comprising the step
of overdeforming the alloy a second time by applying a
stress sufficient to cause nonrecoverable strain in the
alloy wherein the second overdeforming takes place at a
second temperature which is different from the first
temperature, and is preferably room temperature.

11. A method according to any preceding Claim, further
comprising the step of heating the alloy to a
temperature greater than about A_S' preferably greater
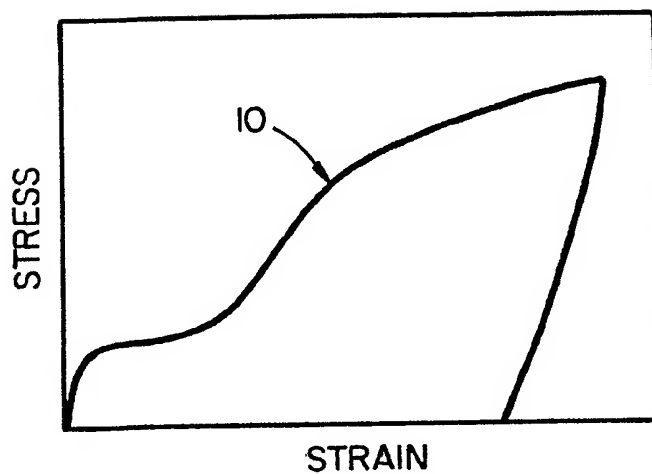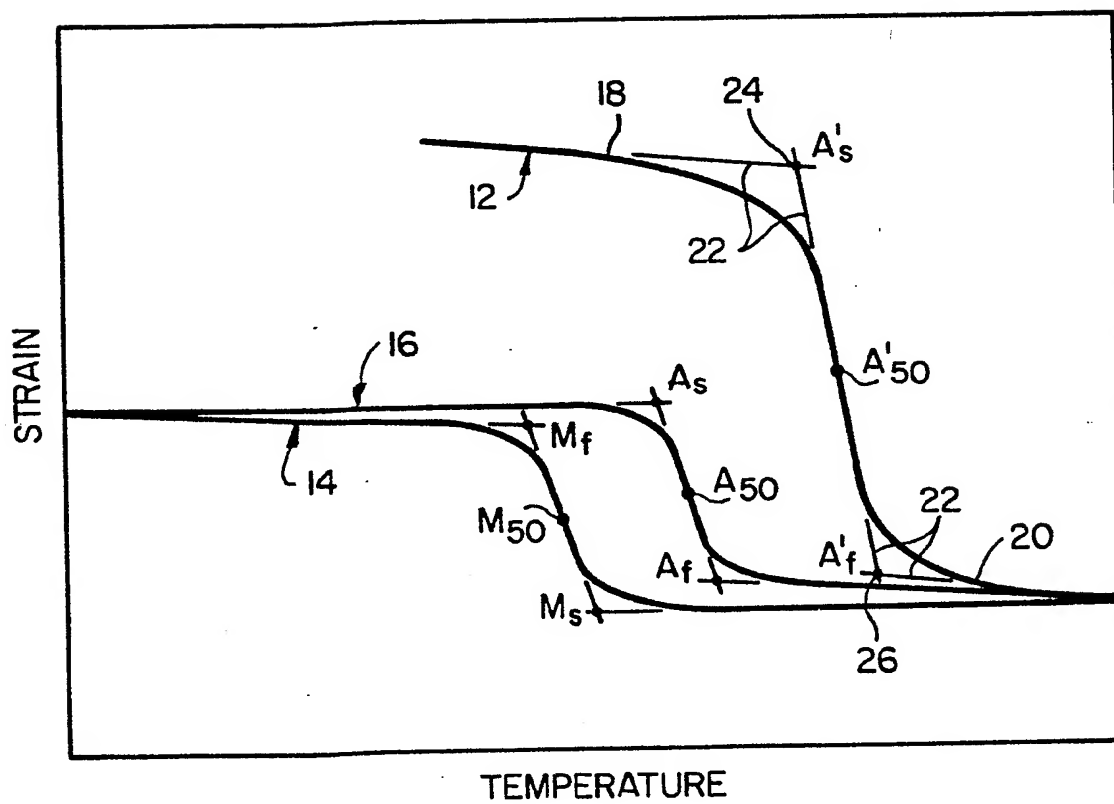than about A_f', so as to effect at least partial
recovery of the alloy.

12. A method according to any preceding Claim, wherein
the nickel/titanium-based shape memory alloy has an M_S
less than about 0°C.

13. A method according to any preceding Claim, wherein
the nickel/titanium-based shape memory alloy is stable,
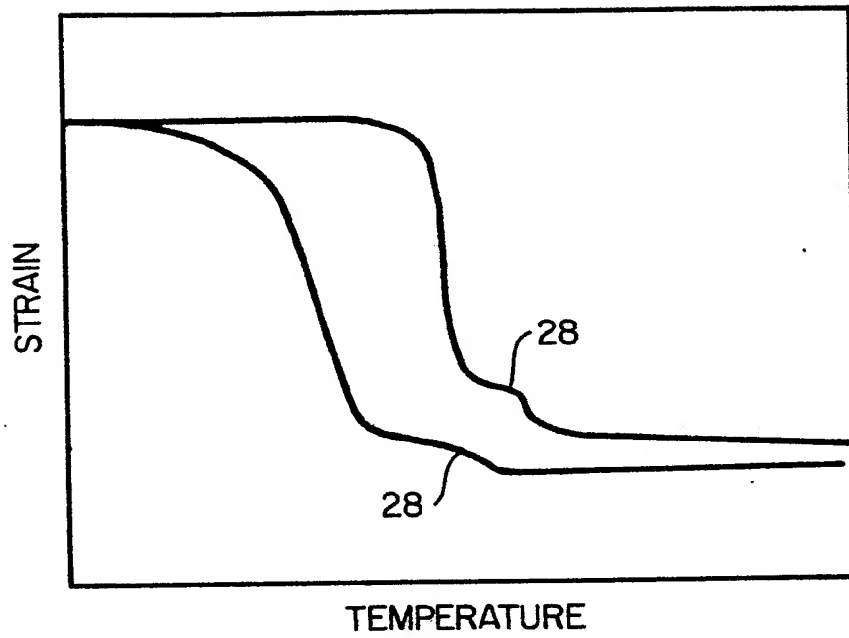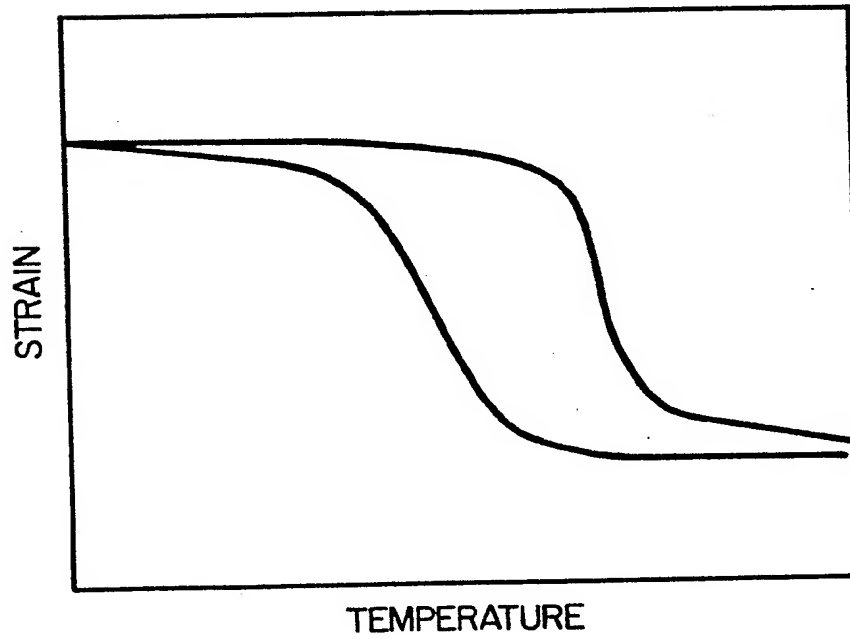does not contain an R phase.

14. A method according to any preceding Claim, wherein the nickel/titanium-based shape memory alloy is (a) a binary alloy, or (b) at least a ternary alloy, preferably a ternary nickel/titanium-based shape memory alloy which consists essentially of nickel, titanium at at least one other element selected from the group consisting of iron, cobalt, vanadium, aluminum, and niobium.
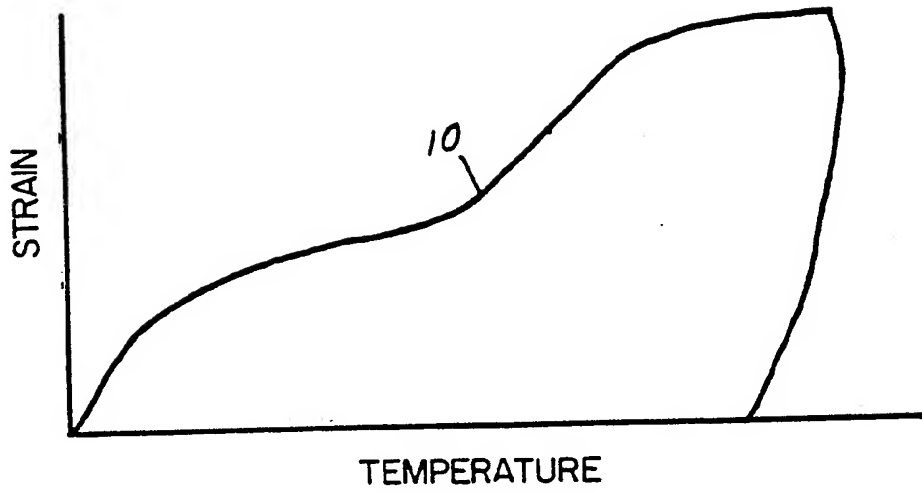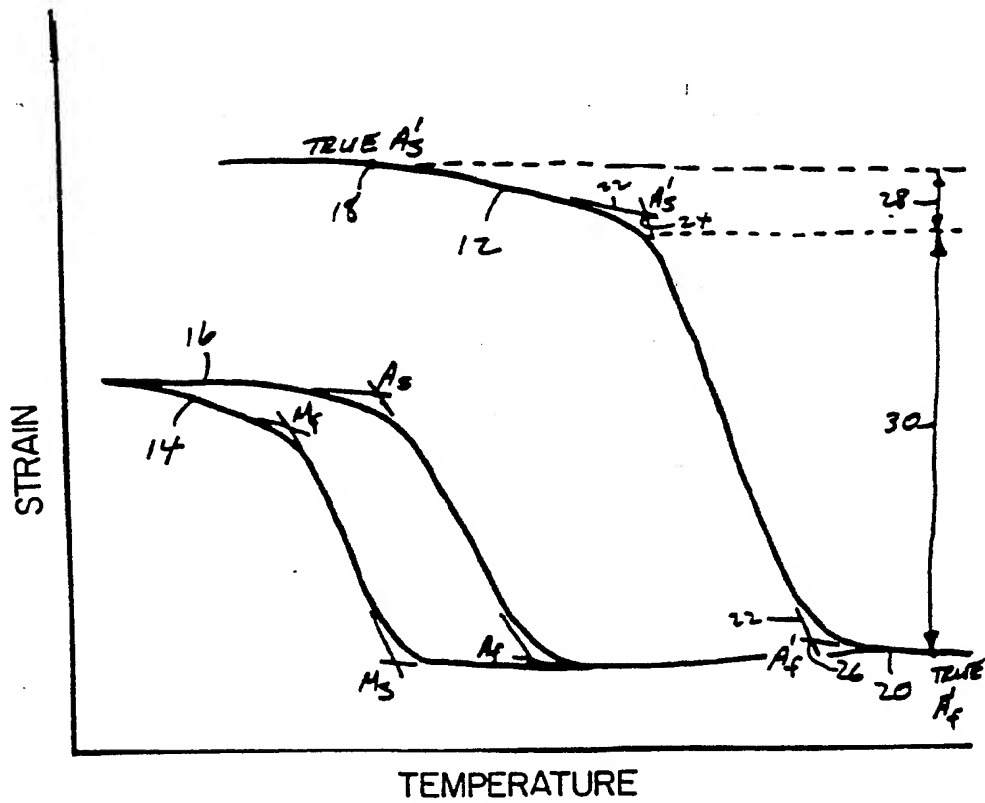
5

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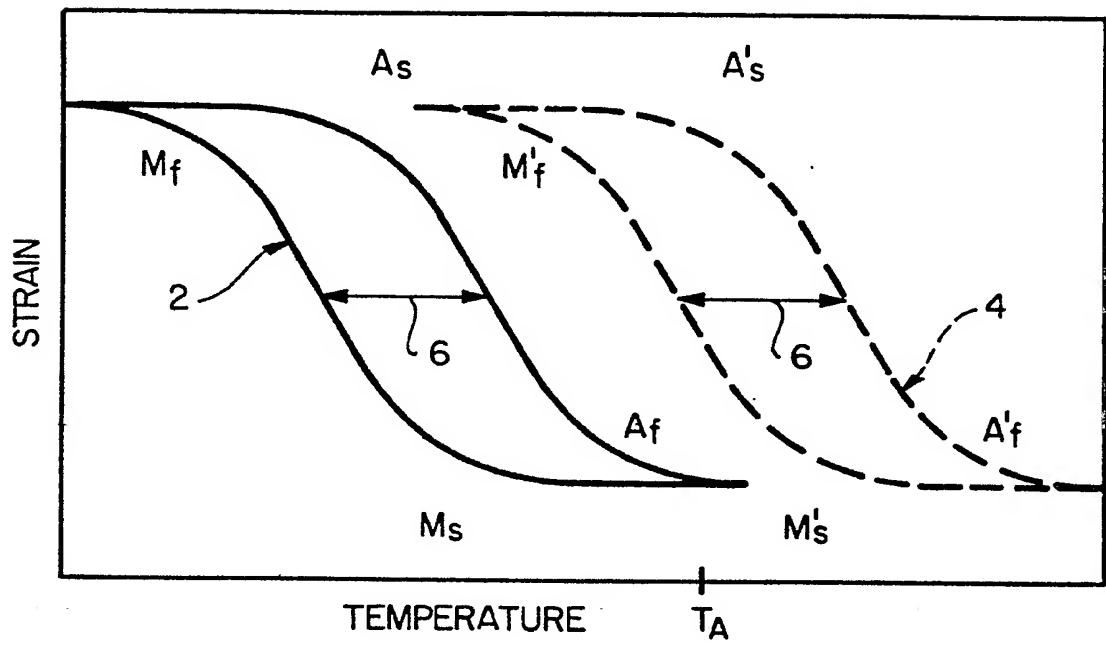
FIG_1
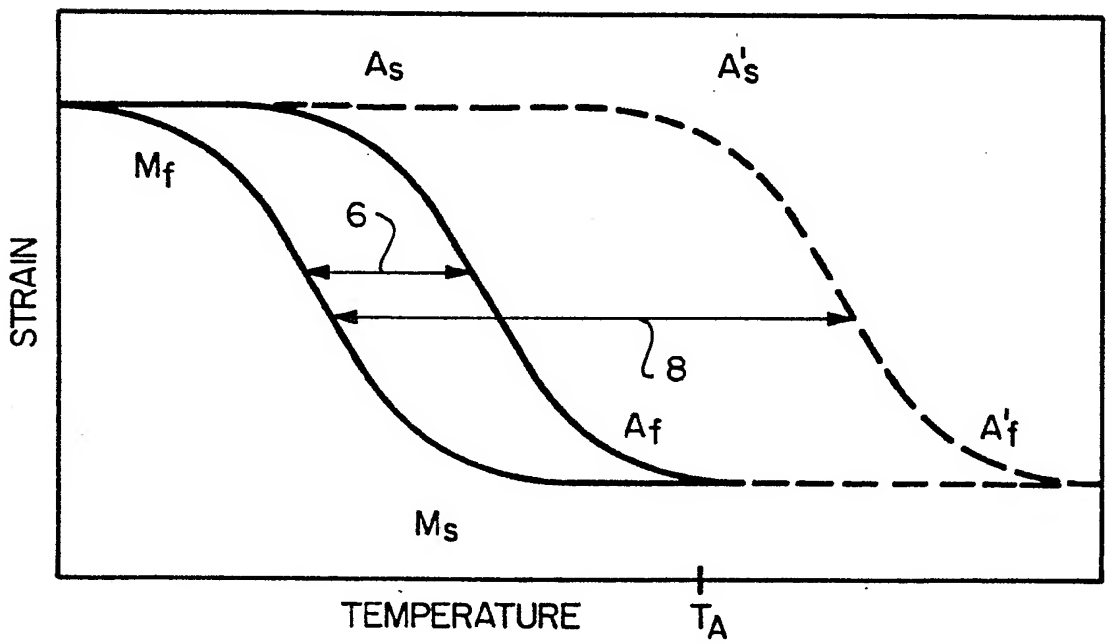
FIG_2

FIG_3

FIG_4

FIG_5

FIG_6

FIG _ 7

FIG _ 8